



UNITED STATES PATENT AND TRADEMARK OFFICE

COMMISSIONER FOR PATENTS
UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. 20231
www.uspto.gov

APPLICATION NUMBER	FILING DATE	GRP ART UNIT	FIL FEE REC'D	ATTY. DOCKET NO.	DRAWINGS	TOT CLAIMS	IND CLAIMS
09/857,287	06/01/2001	1762	860	A34320- PCT-U	4	13	2

CONFIRMATION NO. 9686

FILING RECEIPT



OC000000006342575

Marta E Delsignore
Baker Botts
30 Rockefeller Plaza
New York, NY 10112-0228

Date Mailed: 07/25/2001

Receipt is acknowledged of this nonprovisional Patent Application. It will be considered in its order and you will be notified as to the results of the examination. Be sure to provide the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION when inquiring about this application. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. If an error is noted on this Filing Receipt, please write to the Office of Initial Patent Examination's Customer Service Center. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections (if appropriate).

Applicant(s)

Poopathy Kathirgamanathan, Middlesex, UNITED KINGDOM;

Domestic Priority data as claimed by applicant

THIS APPLICATION IS A 371 OF PCT/GB99/04030 12/01/1999

Foreign Applications

UNITED KINGDOM 9826405.4 12/02/1998

Projected Publication Date: N/A

Non-Publication Request: No

Early Publication Request: No

Title

Method for forming films or layers

Preliminary Class

PCT/GB99/04030

01 JUL 30 PM 3: 06

427

Data entry by : NGUYEN, SON

Team : OIPE

Date: 07/25/2001



**LICENSE FOR FOREIGN FILING UNDER
Title 35, United States Code, Section 184
Title 37, Code of Federal Regulations, 5.11 & 5.15**

GRANTED

The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Office of Export Administration, Department of Commerce (15 CFR 370.10 (j)); the Office of Foreign Assets Control, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15 (b).

PLEASE NOTE the following information about the Filing Receipt:

- The articles such as "a," "an" and "the" are not included as the first words in the title of an application. They are considered to be unnecessary to the understanding of the title.
- The words "new," "improved," "improvements in" or "relating to" are not included as first words in the title of an application because a patent application, by nature, is a new idea or improvement.
- The title may be truncated if it consists of more than 500 characters (letters and spaces combined).
- The docket number allows a maximum of 25 characters.
- If your application was submitted under 37 CFR 1.10, your filing date should be the "date in" found on the Express Mail label. If there is a discrepancy, you should submit a request for a corrected Filing Receipt along with a copy of the Express Mail label showing the "date in."
- The title is recorded in sentence case.

Any corrections that may need to be done to your Filing Receipt should be directed to:

Assistant Commissioner for Patents
Office of Initial Patent Examination
Customer Service Center
Washington, DC 20231

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C09K 11/06, C23C 14/12, B05D 7/24, H05B 33/14	A1	(11) International Publication Number: WO 00/32719 (43) International Publication Date: 8 June 2000 (08.06.00)
(21) International Application Number: PCT/GB99/04030 (22) International Filing Date: 1 December 1999 (01.12.99) (30) Priority Data: 9826405.4 2 December 1998 (02.12.98) GB (71) Applicant (for all designated States except US): SOUTH BANK UNIVERSITY ENTERPRISES LTD. [GB/GB]; 103 Borough Road, London SE1 0AA (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): KATHIRGAMANATHAN, Poopathy [GB/GB]; 14 Sandhurst Avenue, North Harrow, Middlesex HA2 7AP (GB). (74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Westerham, Kent TN16 2BB (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
(54) Title: METHOD FOR FORMING FILMS OR LAYERS		
(57) Abstract An improved method for forming films of organo-metallic complexes in which an organic complex and a labile metal salt are vaporised together or sequentially and the vapour condensed on to a substrate to form a film or layer of the organo-metallic complex on the substrate. The method produces electroluminescent films with improved performance.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakhstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LJ	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

- 1 -

Method for Forming Films or Layers

The present invention relates to a method of forming films or layers of organo-metallic complexes and more particularly it relates to a method of forming organo-metallic complexes and depositing them on a substrate.

When forming a complex of an organic ligand and a metal, a salt of the metal and the organic ligand are reacted together under the appropriate conditions in solution in a suitable solvent. A very large number of reactions are well known and a very large number of organo-metallic complexes are known and are formed by this process.

A particular class of organo-metallic complexes are formed from transition metals, lanthanides and actinides and these complexes have a very large range of applications in catalysis, electrical and electronic devices etc.

Some organo-metallic complexes have electroluminescent or photoluminescent properties and have been described in an article in Chemistry Letters pp 657-660, 1990 Kido et al and in an article in Applied Physics Letters 65 (17) 24 October 1994 Kido et al but these were unstable in atmospheric conditions and difficult to produce as films.

Photoluminescent complexes which are rare earth chelates which fluoresce in ultra violet radiation are known and A. P. Sinha (Spectroscopy of Inorganic Chemistry Vol. 2 Academic Press 1971) describes several classes of rare earth chelates with various monodentate and bidentate ligands.

Group III A metals and lanthanides and actinides with aromatic complexing agents have been described by G. Kallistratos (Chimica Chronika, New Series, 11, 249-266 (1982)). This reference specifically discloses the Eu(III), Tb(III) and U(III) complexes of diphenyl-phosponamidotriphenyl-phosphoran.

EP 0744451A1 also discloses fluorescent chelates of transition or lanthanide or actinide metals.

5 When forming an electroluminescent or photoluminescent device which incorporates an organo-metallic complex as the electroluminescent or photoluminescent active material, a film of the electroluminescent or photoluminescent compound has to be formed on a substrate. This is normally done by deposition of the compound from solution onto the substrate so as to obtain a film or layer of the right thickness etc.

10

The organo-metallic complex can be formed in solution and deposited from this solution or it can be separated and dissolved in another solvent and deposited from this solution etc. or it can be formed by vacuum evaporation of the solid material.

15 We have invented an improved method of forming a film or layer of an organo-metallic complex on a substrate which does not require a solution to be formed nor does it require multiple syntheses.

20 According to the invention there is provided a method for forming a film or layer of an organo-metallic complex on a substrate which method comprises vaporising a metal compound and vaporising an organic complex and condensing the vapour on to a substrate to form a film or layer of the organo-metallic complex on the substrate.

25 In one embodiment the invention comprises mixing a powder comprising a metal compound with a powder comprising an organic complex, heating the mixture formed under a vacuum so that the mixture is vaporised and condensing the vapour on to a substrate to form a film or layer of the organo-metallic complex on the substrate.

30 In another embodiment of the invention the metal compound and the organic complex

- 3 -

are vaporised sequentially.

The term vaporised includes all forms of going from the solid state to the vapour or gaseous state such sublimation etc.

5

The invention is particularly useful with transition metals, lanthanides and actinides which can form stable and useful complexes with organic ligands by this method.

10 The metal preferably is in the form of a salt such as a halide e.g. chloride or bromide which is labile so that it can be vaporised or sublimed, or an organo-metallic compound e.g. diketo complexes, acetyl acetonates, although any metal compound which will vaporise under the conditions can be used.

15 The invention is particularly useful for the preparation of films or layers of photoluminescent and electroluminescent compounds including those incorporating lanthanides or actinides such as samarium, dysprosium, lutetium, thorium, yttrium, gadolinium, europium, terbium, uranium and cerium in the appropriate valence states. Any metal ion having an unfilled inner shell can be used as the metal and the preferred metals are Sm(III), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd(III), Eu(II),
20 Ce(III), Gd(III), U(III), $\text{UO}_2(\text{VI})$, Th(III), as well as metals with an incomplete inner shell e.g. Th(IV), Y(III), La(III), Ce(IV).

25 Mixtures of more than one metal compound and more than one organic complex can be used to obtain a range of mixed organo-metallic complexes. This can be achieved by mixing the compounds before vaporisation or by vaporising the compounds sequentially so as to obtain a multilayered or a mixed layer comprising organo-metallic complexes.

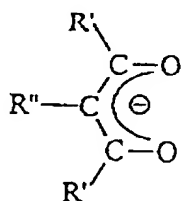
30 In another embodiment of the invention the metal compound can be deposited on the substrate and then a mixture of the metal compound and the organic compound

- 4 -

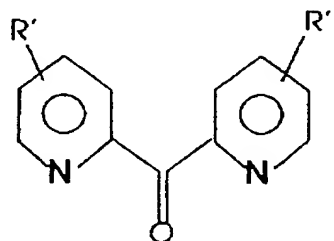
deposited by vaporisation of a mixture of these to obtain various types of layered structures.

5 The organic ligands in the organo-metallic complex formed can be any organic complex which can react with the metal compound to form an organo-metallic complex or which, when co-deposited with the organic complex forms an organo-metallic complex. It may be, particularly with sequential deposition that the organo-metal complex formed has a variable composition through the layer.

10 The organic ligands which can be used include



or

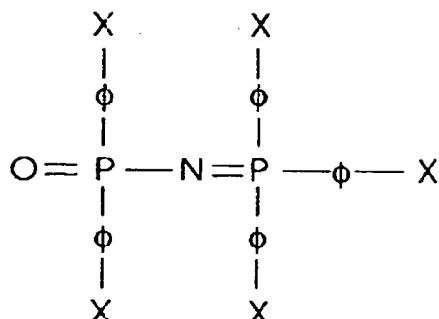


15 where R' is the same or different at different parts of the molecule and each R'' and R' is a hydrocarbyl group e.g. alkyl, a substituted or unsubstituted aromatic or heterocyclic ring structure a fluorocarbon or R'' is -CF₃ or hydrogen or R'' is copolymerised with a monomer e.g. or R' is t-butyl and R'' hydrogen.

Preferably each of R', R'', and R' is an alkyl group preferably a -C(CH₃) group,

20 or

- 5 -



where X can be the same or different in each case and can be H, F, Me, Et, OMe, or OEt.

5

Preferred organic complexes are 2,2,6,6-tetramethyl-3,5-heptanedionato(TMHD); α , α' , α'' tripyridyl, dibenzoyl methane(DBM), diphenylphosphonimide triphenyl phosphorane(OPNP), bathophen (4,7-diphenyl-1,10-phenanthroline), 1,10 phenanthroline (Phen) and crown ethers, cryptands, substituted calix(4)arene based ligands and other organic complexes

Particularly preferred organo-metallic complexes are the Th, Y, Eu, Dy, and SM complexes of tripyridyl and TMHD and complexes such as thorium bathophen, yttrium tripyridyl and TMHD, and europium (III) (TMHD)₃ complexes, terbium (TMHD)₃OPNP, europium (II) (TMHD)₂ and europium (II) (TMHD)₂ OPNP.

The organic complex used to form the organo-metallic complex should be in a form which is stable in powder form under the conditions of the vaporisation, for organic complexes which are unstable in oxygen an inert atmosphere can be used.

20

When mixed powders of the metal compound and the organic complex are vaporised they should be of a size such that intimate mixing can take place. compounds can be bought commercially in powder form and these are often suitable without further treatment, if smaller size particles are required, the starting material can be ground. If

the organic complex is formed by precipitation from a solution this can be formed as a powder which, after drying, can be mixed with the metal compound.

5 In one embodiment of the invention an organo-metallic complex such as a complex of a transition metal, lanthanide or actinide and any of the above specified organic ligands is mixed with an organic complex e.g. as referred to above and the resultant mixture heated in vacuum to vaporise the mixture and to deposit the organo metal complex formed onto a substrate.

10 In another embodiment of the invention an organo-metallic complex such as a complex of a transition metal, lanthanide or actinide and any of the above specified organic ligands is heated in vacuum to vaporise the mixture and to deposit the organo- metallic complex on the substrate and then an organic complex e.g. as referred to above and is heated in vacuum to vaporise the complex and to deposit it
15 on top of the organo-metallic compound to form the organo-metal complex layer on the substrate.

The starting materials should be dry and, if necessary they can be dried prior to heating to remove any water or other liquid compounds.

20

The vaporisation takes place under a vacuum which is preferably below 10^{-5} torr and more preferably below 10^{-6} torr.

25 The metal compound and the organic complex or a mixture of these can be placed in a suitable coater. the temperature is not critical but should be sufficient to vaporise or sublime the mixture. Temperatures above 100°C and up to 250°C and higher can be used.

The vapour is then condensed or deposited onto a substrate which is held at a lower

- 7 -

temperature as in conventional vapour deposition processes e.g. chemical vapour deposition, vacuum coating, electron beam coating etc.

5 The substrate which can be used will depend for the purposes for which the device is to be used, as the substrate need not be subjected to heating conventional substrates can be used.

10 The method is particularly useful in forming electroluminescent devices in which a layer of an electroluminescent compound is deposited on to a conductive substrate optionally with other layers such as layers of hole transporting compounds and electron transporting compounds to arrive a multilayered structure in which an anode and cathode are attached to form an electroluminescent device.

15 In a typical electroluminescent device there is a transparent substrate which is a glass or plastic material which acts as the anode, preferred substrates are conductive glasses such as indium tin oxide coated glass, but any glass which is conductive or has a conductive layer can be used. The electroluminescent material can be deposited on the substrate by the method of the invention or preferably there can be a hole transporting layer deposited on the transparent substrate and the electroluminescent material is deposited on the hole transporting layer. The hole transporting layer serves to transport holes and to block the electrons, thus preventing electrons from moving into the electrode without recombining with holes. The recombination of carriers therefore mainly takes place in the emitter layer.

25 Hole transporting layers are used in polymer electroluminescent devices and any of the known hole transporting materials in film form can be used.

30 The hole transporting layer can be made of a film of an aromatic amine complex such as poly(vinylcarbazole), N,N'-diphenyl-N,N'-bis (3-methylphenyl) -1,1' -biphenyl -4,4'-diamine (TPD) or polyaniline.

There is preferably an electron transporting layer between the cathode and the electroluminescent layer. This electron transporting layer can be a metal complex such as a metal quinolate e.g. an aluminium quinolate which will transport electrons
5 when an electric current is passed through it or an organic compound such as PBD or a polymer e.g. containing cyano groups. The cathode can be any metal.

In a preferred structure there is a substrate formed of a transparent conductive material which is the anode on which is successively deposited a hole transportation
10 layer, the electroluminescent layer and an electron transporting layer which is connected to the cathode.

Optionally dyes such as fluorescent laser dyes, luminescent laser dyes can be included to modify the colour spectrum of the emitted light and also enhance the
15 photoluminescent and electroluminescent efficiencies.

The thickness of the layer deposited on the substrate by the method of the invention can be varied according to the conditions of the vaporisation and deposition and in general layers of from one molecule thick up to any desired thickness can be formed.
20

It has been surprisingly found that for electroluminescent and photoluminescent organo-metallic complexes formed by the method of the invention have superior properties to those complexes where the formed organo-metallic complex is deposited on a substrate from a solution e.g. by evaporation or spin deposition. The
25 reason for this is not known and was unexpected.

Types of electroluminescent devices are shown in figs 1a, 1b, 1c and 1d of the drawings in which (1) is layer deposited in accordance with the invention, (2) is ITO, (3) is an electron transporting layer (4) is a hole transporting layer and (5) is an
30 electron transporting layer. The invention enables a emissive layer to be deposited on

- 9 -

ITO or on to a layer previously applied to the ITO.

Examples.

- 5 Thin films were made according to the invention and compared with films made by chemical synthesis. The Photoluminescence (PL) Efficiency and colour were measured and the results shown in Table 1. The colour was measured using colour chart CIE I931.

10 Example 1

Thin film Tb(TMHD)₃ OPNP

- (i) 50mg of Tb(TMHD)₃ (7×10^{-5} moles) and 33.68mg of OPNP (7.05×10^{-5} moles) were
15 ground together in a mortar and pestle and a 3mg portion was placed on a molybdenum boat in an Edwards(E306) vacuum coater. Spectrosil slides (UVgrade) were secured on a sample holder. The vacuum coater was evacuated to 10^{-7} torr and the sample was heated using an electrical heater at 10 to 90 A and 10V for up to twenty seconds to give a film of Tb(TMHD)₃ OPNP.

- 20 Comparative experiments were carried out on (ii) a film of Tb(TMHD)₃ OPNP (3 mg) pre-synthesised from a solution and (iii) and a film of Tb(TMHD)₃ (3mg) purchased from Strem chemicals, Cambridge. The spectra are shown in fig. 3.

Example 2Thin Film $\text{Eu}(\text{DBM})_3 \cdot \text{OPNP}$

5 (i) 50mg of $\text{Eu}(\text{DBM})_3$ (6×10^{-5} moles) was mixed with 57.43mg of OPNP (1.2×10^{-4} moles) and ground in a mortar and pestle. The mixture was evaporated as in Example 1 to form a film of $\text{Eu}(\text{DBM})_3 (\text{OPNP})_n$.

(ii) A Comparative experiment was carried out on a chemically synthesised film of
10 $\text{Eu}(\text{DBM})_3 (\text{OPNP})_n$. The spectra are shown in fig. 4.

Table 1

15	Example	System	Relative PL Efficiency	CIE(x)	CIE(y)
	1(i)	$\text{Tb}(\text{TMHD})_3 \cdot \text{OPNP}(50\text{nm})$	2	0.35	0.58
	1(ii)	$\text{Tb}(\text{TMHD})_3 \cdot \text{OPNP}(40\text{nm})$	1	0.35	0.69
20	1(iii)	$\text{Tb}(\text{TMHD})_3 (50\text{nm})$	1×10^{-3}	0.29	0.62
	2(i)	$\text{Eu}(\text{DBM})_3 \cdot \text{OPNP}_n(50\text{nm})$	1.4	0.62	0.32
	2(ii)	$\text{Eu}(\text{DBM})_3 \cdot \text{OPNP}_n (50\text{nm})$	1	0.58	0.30

Example 3Fabrication of an Electroluminescent Devices Based on $\text{Tb}(\text{TMHD})_3$ OPNP

5 (i) A 3mg mixture of $\text{Tb}(\text{TMHD})_3$ OPNP prepared as in Example 1 was evaporated onto a patterned ITO electrode to give a film of 50 nm thickness. The patterned ITO had been previously coated with 20 nm of a hole transporting layer formed of TPD. Aluminium quinolate (Alq_3) was then evaporated on top the layer give a film of 20nm thickness to act as an electron-transporting layer. An aluminium top contact
10 (900 nm) was made to form the structure of fig. 2 of the drawings.

(ii) A comparative experiment was carried out using the same structure and configuration but using a chemically synthesised $\text{Tb}(\text{TMHD})_3$ OPNP.

15 The luminous efficiency was measured and the results shown in Table 3.

Table 3

20	System	Normalised Absolute Efficiency ($\eta/\text{lm w}^{-1}$)
	(i) $\text{Tb}(\text{TMHD})_3$ OPNP	6.0
	(ii) $\text{Tb}(\text{TMHD})_3$ OPNP	1.0

25 As can be seen the device based on a film formed by the method of the invention has a much higher luminous efficiency.

Example 4Fabrication of an Electroluminescent Device Based on $\text{Eu}(\text{DBM})_3\text{Phen}$

- 5 The structure of Example 4 was fabricated using an equimolar mixture of $\text{Eu}(\text{DBM})_3$ and 1,10 Phenanthroline in place of the $\text{Tb}(\text{TMIID})_3\text{OPNP}$ so as to form a film of $\text{Eu}(\text{DBM})_3\text{Phen}$. The experimental conditions and the structural configuration were as in example 4
- 10 The luminous efficiency was measured and the results shown in Table 4.

Table 4

15	System	Normalised Absolute Efficiency
		$(\eta/\text{lm w}^{-1})$
	(i) $\text{Eu}(\text{DBM})_3\text{Phen}$	1.1
	(ii) $\text{Eu}(\text{DBM})_3\text{Phen}$	1.0

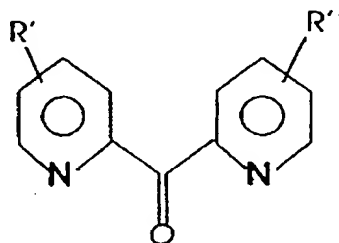
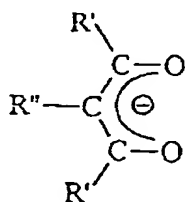
- 20 As can be seen the device based on a film formed by the method of the invention has a 10% higher luminous efficiency.

Claims

1. A method for forming a film or layer of an organo-metallic complex on a substrate which method comprises vaporising a metal compound and vaporising an organic complex and condensing the vapour on to a substrate to form a film or layer of the organo-metallic complex on the substrate.
5
2. A method as claimed in claim 1 which comprises mixing a powder comprising a metal compound with a powder comprising an organic complex, heating the mixture formed so that the mixture is vaporised and condensing the vapour on to a substrate to form a film or layer of the organo-metallic complex on the substrate.
10
3. An electroluminescent device as claimed in claim 1 in which the metal compound and the organic complex are vaporised sequentially.
15
4. A method as claimed in claim any one of claims 1 to 3 in which the metal compound is a labile salt of a metal selected from transition metals, lanthanides and actinides or selected from labile organo-metallic compound of transition metals, lanthanides and actinides.
20
5. A method as claimed in claim 4 in which the metal is Sm(III), Eu(III), Tb(III), Dy(III), Yb(III), Lu(III), Gd (III), Eu(II), CE(III), Gd(III) U(III), UO₂(VI), Th(III), Th(IV), Y(III), La(III) or Ce(IV).
25
6. A method as claimed in any one of claims 1 to 5 in which mixtures of more than one metal compound and more than one organic complex are vaporised to obtain a mixed organo-metallic complex.
30
7. A method as claimed in claim 6 in which the compounds are mixed before vaporisation.

- 14 -

8. A method as claimed in claim 6 in which the compounds vaporised sequentially so as to obtain a multilayered or a mixed layer comprising organo-metallic complexes.
- 5 9. A method as claimed in claim 6 in which the metal compound is deposited on the substrate and then a mixture of the metal compound and the organic compound deposited by vaporisation of a mixture of these to obtain a layered structures.
- 10 10. A method as claimed in any one of the preceding claims in which the organic complex incorporates a moiety of formula

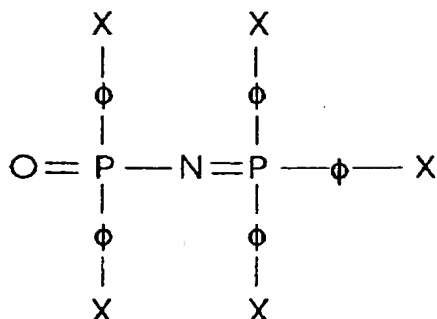


or

- 15 where R' is the same or different at different parts of the molecule and each R' ' and R' is a hydrocarbyl group e.g. alkyl, a substituted or unsubstituted aromatic or heterocyclic ring structure a fluorocarbon or R' ' is -CF₃ or hydrogen or R' ' is copolymerised with a monomer e.g. or R' is t-butyl and R' ' hydrogen.
- or

20

- 15 -



where X can be the same or different in each case and can be H, F, Me, Et, OMe, or OEt.

5

11. A method as claimed in claim 10 in which each of R', R'', and R' is an alkyl group.

10

12. A method as claimed in claim 10 in which the organic complex is selected from 2,2,6,6-tetramethyl-3,5-heptanedionato(TMHD); α' , α'' , α''' tripyridyl, dibenzoyl methane(DBM), diphenylphosphonimide triphenyl phosphorane(OPNP), bathophen (4,7-diphenyl-1,1-phenanthroline), 1,10 phenanthroline (Phen) and crown ethers, cryptands, substituted calix(4)arene based ligands and other organic complexes

15

13. A method as claimed in claim 10, 11 or 12 in which the organo-metallic complexes is selected from the Th, Y, Eu, Dy, and Sm complexes of tripyridyl and TMDH and thorium bathophen, yttrium tripyridyl and TMHD, and europium (III) (TMHD)₃ complexes, terbium (TMHD)₃OPNP, europium (II) (TMHD)₂ and europium (II) (TMHD)₂ OPNP.

20

14. A method for forming electroluminescent devices in which a layer of an electroluminescent compound is deposited on to a conductive substrate by the method of any one of the preceding claims.

1/4

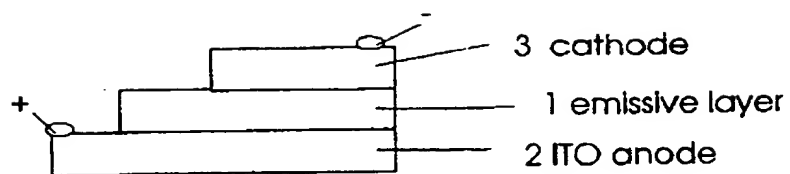


Fig. 1a

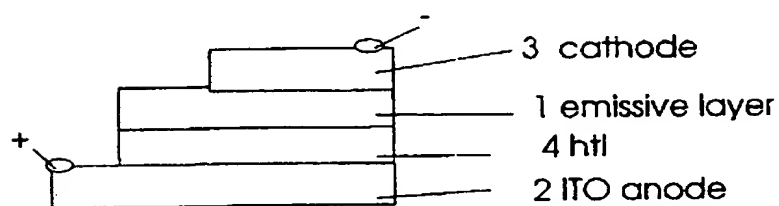


Fig. 1b

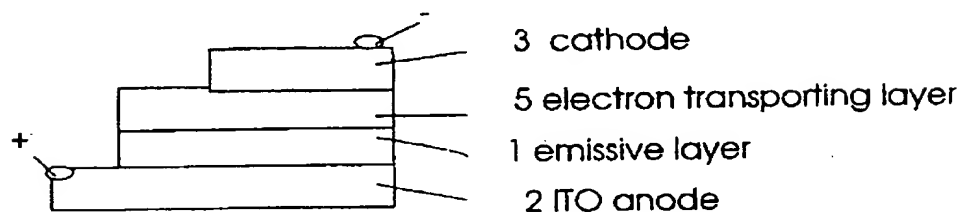


Fig. 1c

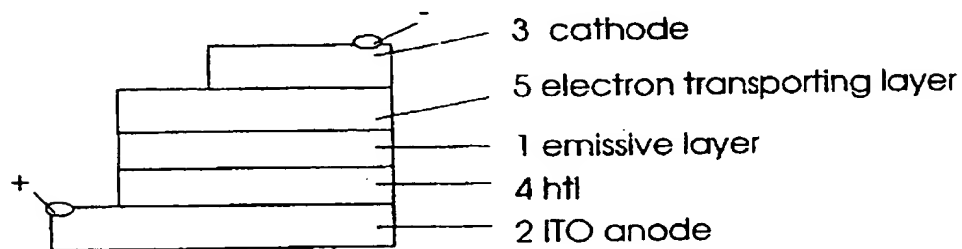


Fig. 1d

2/4

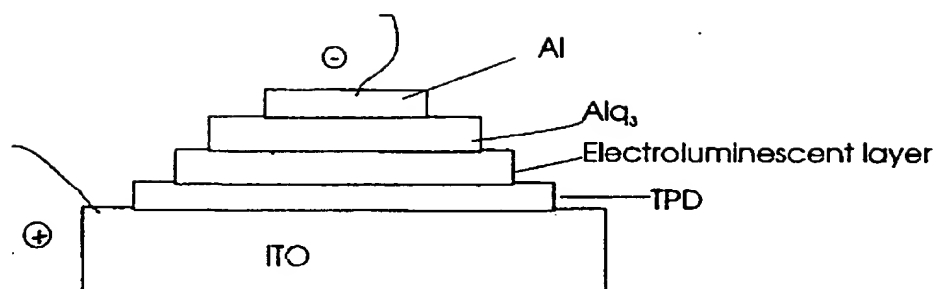


Fig. 2

3/4

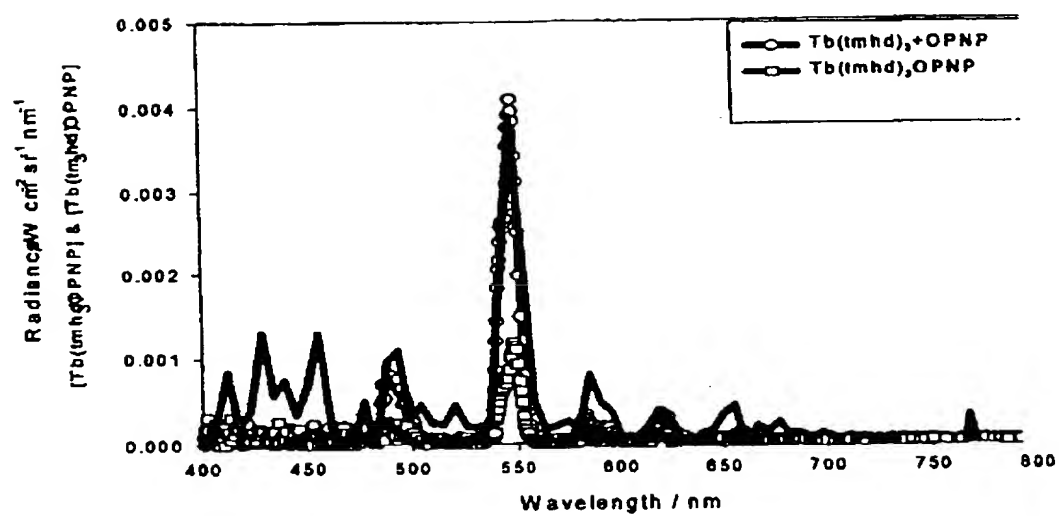


Fig. 3

4/4

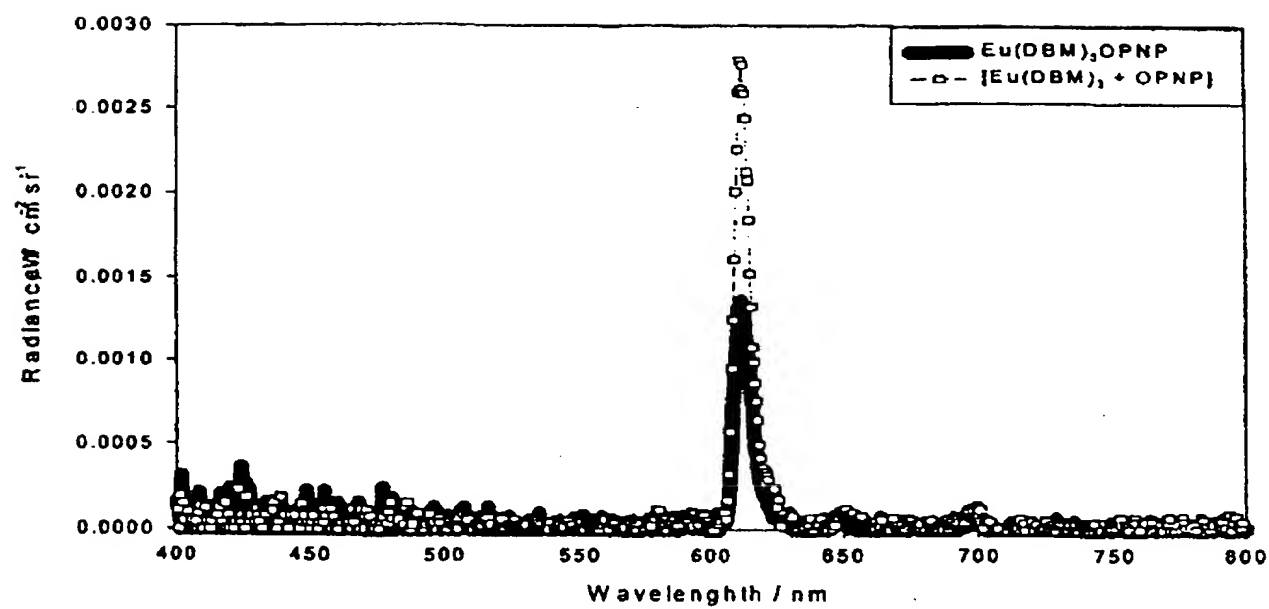


Fig. 4